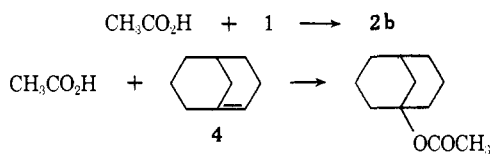


drop of 70% perchloric acid afforded the hemiketal **2a**, and reaction of **1** with acetic acid gave exclusively acetate **2b**.⁹ Hydrogenation of **1** (5% Pd-C in 20 ml of ethanol with 2 drops of acetic acid) afforded 9-oxabicyclo[3.3.1]nonane (**2g**).¹⁷

Comparisons of the chemical reactivity of **1** have proved interesting. Whereas the half-life of the reaction of **1** with acetic acid at 25° is 68 hr, the reaction of bicyclo[3.3.1]non-1-ene (**4**)^{3a} with acetic acid at 25°



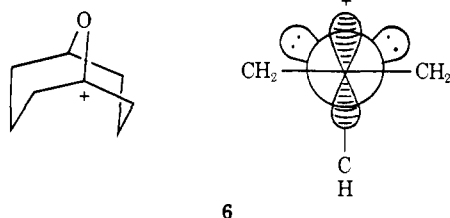
is complete in 2 min ($t_{1/2} < 1$ min). The hydrocarbon **4** is at least 4000 times as reactive as the enol ether **1**, just the opposite of the case for unstrained compounds where enol ethers are vastly more reactive.

Similarly, we have compared the rate of perchloric acid-catalyzed hydrolysis (and ethanolysis) of **1** in 95% aqueous ethanol with that of 1-ethoxycyclohexene (**5**);¹⁸ see Table I. Enol ether **5** is 10⁵ times as reactive as the

Table I. Rates of Hydrolysis of Enol Ethers

		k_2 , l. mol ⁻¹ sec ⁻¹
$\mathbf{1} \xrightarrow[\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}]{\text{HClO}_4} \mathbf{2a} + \mathbf{2c}$		8.8×10^{-4} (27°)
$\mathbf{5} \xrightarrow[\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}]{\text{HClO}_4} \text{Cyclohexene} + \text{C}_2\text{H}_5\text{OH}$		8.0×10^1 (25°) ¹

enol ether **1**, in spite of the strain energy of **1** which should accelerate its reaction. We attribute the low reactivity of **1** in these reactions to inhibition of resonance of the bridging oxygen atom with the positive bridgehead carbon in cation **6**. The bridging oxygen



atom is assumed to have distorted tetrahedral geometry as shown in the projection view of **6** along the 1-9 bond. In a strain-free model the empty p orbital at the bridgehead carbon bisects the angle between the oxygen orbitals containing the nonbonding electrons. The strain energy of **1** may be estimated as approximately 12 kcal/mol,¹⁹ relative to **2a**, while cation **6** should be nearly strainless.²⁰ If the strain of **1** is relieved entirely at the transition state for protonation, the rate of the reaction

(17) F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

(18) Rates are first order in both acid and enol ether and were measured spectrophotometrically at 208 nm. Rates for **5** are from A. J. Kresge, H. L. Chen, Y. Chiang, E. Murrill, M. A. Payne, and D. S. Sagatys, *ibid.*, **93**, 413 (1971).

(19) The strain energy of **4** is 12 kcal/mol. P. M. Lesko and R. B. Turner, *ibid.*, **90**, 6888 (1968). The strain energy of **1** is unknown. See also N. L. Allinger and J. T. Sprague, *ibid.*, **94**, 5734 (1972).

(20) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).

should be accelerated by approximately 10⁹. Therefore, the real rate retardation seen in comparing the rates of hydrolysis of **1** and **5** may be as great as 10¹⁴.

Finally, we have compared the rates of solvolysis of 1-chlorobicyclo[3.3.1]nonane (**7**)²⁰ and 1-chloro-9-oxabicyclo[3.3.1]nonane²¹ in 60% aqueous ethanol. The results, summarized in Table II, show that some reso-

Table II. Rates of Solvolysis of Bridgehead Chlorides in 60% Aqueous Ethanol

		Temp, °C	k_1 , ^a sec ⁻¹ × 10 ⁵
	(7)	65.10	21.8
		55.00	6.83
		44.85	2.11
	(2f)	65.05	6.43
		55.00	2.08
		44.85	0.646

^a The rates for **7** are in good agreement with earlier work.²⁰

nance must still persist in cation **6** since the inductive effect of oxygen should retard the reaction by more than a factor of 3.²²

(21) Prepared from **2a** with thionyl chloride.

(22) See H. Stetter, P. Tacke, and J. Gartner, *Chem. Ber.*, **97**, 3480 (1964), for a similar comparison in the adamantyl ring system.

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Reaction of Carbon Vapor with Lithium Atoms. A Direct Synthesis of Polyolithium Compounds

Sir:

The reaction of lithium atoms with chlorocarbons has been shown to produce tetralithiomethane and hexalithioethane from analogous chlorocarbon starting materials.¹ It is well known that carbon vapor, usually produced with a carbon arc or by vaporizing carbon with a laser, consists of the carbon species C¹ through C₆² with C₃ in highest concentration. Carbon vapor is known to be reactive.³ A study of the reaction of atomic lithium with carbon vapor species was therefore deemed worthwhile since it was very unlikely that these reactive species would combine to give only lithium carbide C₂Li₂.

A stainless steel reactor was used (Figure 1) in which carbon vapor was generated by an arc between movable graphite electrodes positioned at the orifice of the lithium Knudsen cell. The reaction vessel was evacuated to 10⁻⁵ Torr, and the Knudsen cell, containing 11 g of lithium, was heated to 800-850° by induction or resistance heating. The lower walls of the reactor were cooled to -196°, and the arc was initiated with an 18-V, 250-A ac source. After 45 min the reaction

(1) C. Chung and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 1078 (1972).

(2) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *J. Chem. Phys.*, **31**, 1131 (1959).

(3) P. S. Skellern and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 1135 (1965).

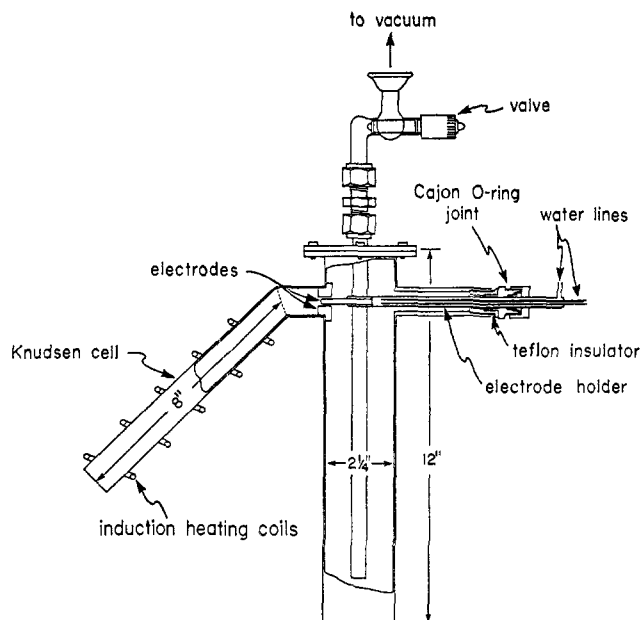


Figure 1.

was terminated. The extremely air- and moisture-sensitive products were handled with care under argon.

The products were hydrolyzed at 0°, passed through a trap at -30° to remove H₂O, and collected at -196°. The yield (gas measurement) of gaseous products averaged 11 mmol/45 min. The hydrolysis products were characterized using a high-resolution double-focusing C.E.C.-21-110B mass spectrometer at 70 eV. Parent ions were observed for CH₄⁺ (16.03133), C₂H₂⁺ (26.01671), C₂H₃⁺ (28.03081), and C₃H₄⁺ (40.03177). The principal product, C₃H₄, ranged from 40 to 65% of the volatile products. Percentage yields of other hydrocarbons were CH₄, 0-10%, and C₂H₂, 10-30%. The yield of C₂H₄ averaged 15%, but occasionally accounted for 45% of the volatile products. Spectroscopic quantities of several higher molecular weight products were also observed.

The principal product, C₃Li₄,⁴ which is known to be soluble in THF, was then derivatized by adding ClSi(Me₃)₃ to a -78° THF solution of the reaction product and warmed while stirring over a 24-hr period. A white compound, C₃(SiMe₃)₄, was recovered and was characterized by its mass and nmr spectra. A parent ion was observed at 328 and a (P - CH₃)⁺ peak occurred at 313 with the appropriate silicon isotopic distributions. The H¹ nmr spectrum of the compound in CCl₄ gave a singlet at τ 9.89 which is in agreement with the spectrum previously reported (τ 9.90) for C₃(SiMe₃)₄.⁴

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(4) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **91**, 6155 (1969); R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965).

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Nuclear Magnetic Resonance Evidence for Stereochemical Rigidity in ML₅ Complexes

Sir:

We wish to report, for the first time, nmr evidence for stereochemical rigidity in an ML₅ complex, {Rh[P(OCH₃)₃]₅}⁺B(C₆H₅)₄⁻. All previous nmr investigations have indicated that the barriers to intramolecular rearrangement in ML₅ compounds are very low, resulting in a rapid exchange of the five ligands. Despite the large body of work concerned with rigidity in five coordination, attempts to observe the inequivalence of the ligands for any ML₅ species in solution (required by all reasonable structures), starting with the early nmr studies of PF₅,¹⁻³ have so far failed.

In molecules such as IF₅, the inequivalence of the fluorine ligands can be observed using nmr;⁴ the barrier to rearrangement is large and the low-temperature limit spectra are not compatible with the idealized structures expected in five coordination (trigonal bipyramid or square pyramid). In accord with the Gillespie-Nyholm rules, we regard these molecules as effectively six-coordinate with the nonbonding electron pair acting as the sixth ligand. In other cases where inequivalence of the ligands can be observed using nmr (such as SbF₅), the molecules are not monomeric in solution.⁵

Confining our attention to group VIII transition metal complexes with d⁸ configurations, we may note that a single resonance was observed in the natural abundance ¹³C spectrum of Fe(CO)₅ at room temperature.⁶ No change was observed in this spectrum on cooling a solution in ether.⁷ We have observed that the ¹³C nmr spectrum of a solution of Fe(CO)₅ in 90% chlorodifluoromethane-10% methylene chloride remains a sharp single line down to ~-170°. More recently we⁸ have recorded the ¹⁹F nmr spectra of Fe(PF₃)₅, Ru(PF₃)₅, and Os(PF₃)₅ down to -160° in chlorodifluoromethane. Again, all five ligands were observed to be equivalent on the nmr time scale.

Our observation that in HM(PF₃)₄ complexes the barrier decreases on going from the neutral species of the cobalt triad to the isoelectronic anions of the iron triad, and that there was a steady increase in barrier on going down a triad,^{8,9} led us to believe that there would be a good chance of observing slow exchange limit nmr spectra for ML₅⁺ cationic species of rhodium or iridium. Rhodium has the additional advantage that its nuclear spin *I* = 1/2 and rhodium to phosphorus couplings are readily observed in ML₅⁺ complexes where L is a trivalent phosphorus ligand. This ligand

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(2) E. L. Muettterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(3) Infrared, Raman, and electron diffraction methods show conclusively that PF₅ has a trigonal-bipyramidal D_{3h} structure.

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(5) C. A. Hoffmann, B. E. Holder, and W. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

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(7) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(8) P. Meakin, E. L. Muettterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5271 (1972).

(9) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muettterties, *ibid.*, **93**, 1797 (1971).